

which a new method was developed, and more than 2,000 wet lead-assays were made by that method, on various ores and under purposely varied conditions, in order to determine the conditions necessary to accuracy, and to test the applicability of the method to all kinds of pure and impure lead ores and products.

"One weakness of the ammonium molybdate method is the end reaction with the indicator—a freshly prepared solution of tannin. The usual practice is to titrate at boiling heat, and, for a high percentage of metal, to make a second boiling after getting a faint end reaction, and then to finish to a complete end tint. The correction for the indicator is, to some extent, affected by the personal equation involved in the operator's conception of a perceptible yellow tint, and varies among different analysts from 0.3 to 0.5 cc. of a standard solution of which 1 cc. equals 10 mg. of lead. It is evident that while this is quite permissible with fair grade ores (and at the same time have different operators check quite closely enough for commercial purposes), it is an entirely different matter in dealing with tailings, containing, say, 0.3 per cent. lead, in which the variation in the correction used for the indicator would represent practically the total quantity of lead present.

"A somewhat extreme instance showing this weakness came under my notice a few months ago. A series of samples of siliceous tailings, carrying from 0.3 to 0.5 per cent. lead, were sent for checking purposes to a leading umpire assaying establishment in the West, with the statement that they were tailings for wet lead-assay. The report was, for about half of the lot, 'trace'; for the remainder, 'none.' The analyst wrote us that the ammonium molybdate method had been used, and that, although he could see fine galena in the tailings, and could even pan it out, he had found, on assaying, that the number of drops of molybdate solution necessary to react with the tannin was in each case no more than the correction amount for indicator; so that he was forced to make the report as he did.

"Assuming that the amount of ammonium acetate used, and the bulk of solution for titration, were at the minimum limits for such fractional percentages, it is probable that if, in these cases, the analyst had given his flasks a prolonged boiling after adding the first few drops of molybdate solution, he would have found that his end tint had faded sufficiently to accommodate a few additional drops of the standard solution. This would have given him, above the indicator requirements, a small fraction which he could then have labeled 'lead.' A result, however, which has to be squeezed out by such labored and uncertain efforts is neither gratifying to the analyst nor really valuable to his client.

"Furthermore, the lead molybdate precipitate being white, and the practice being common among analysts of not pouring the ammonium acetate solution through the sulphates on the filter, but of depositing filter and all in the original flask, digesting therein with ammonium acetate, and then titrating, it follows that, with only slight traces of lead present, there is no proof positive to the eye that the few drops of molybdate added really found any lead to precipitate, the solution being turbid from the slimes of the filter. The analyst is in doubt whether to report, say, 0.2 per cent. of lead, and chance it; to compromise on a 'trace'; or to make a clean sweep and say 'none.' This hypothetical case may be considered by many as overdrawn, but I know from personal experience whereof I speak.

"The other main and commonly occurring weakness of the molybdate method is shown in dealing with ores containing

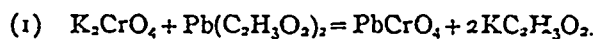
large quantities of lime. Should the percentage of lead be fairly large, say 5 per cent. or more, the molybdate method does very well; but with small and fractional percentages of lead, all the above-cited troubles occur and are aggravated by the tedium of washing the bulky precipitate of pasty calcium sulphate derived from the sulphuric-acid evaporation. Ores of this class are common in south-eastern Missouri; and, although remarkably pure in the sense of containing little else than galena in slightly siliceous dolomite, they have given much trouble to analysts who have to look for fractional percentages of lead in such material.

"Some years ago, having experienced difficulties somewhat analogous to those above mentioned, I gave up the using the molybdate method on material containing less than 1 per cent. of lead, and for some time employed a method of precipitating those small amounts of lead from the hot, filtered ammonium acetate solution (after it had been acidified with hydrochloric acid), on a strip of pure aluminum free from silicon. The precipitated lead was removed from the aluminum strip by rubbing, washed, dried at 110 degrees C., between filter papers, and weighed as metallic lead. This method is tedious if many determinations are to be made, and it possesses several disadvantages, not the least being that, when the quantity of lead present exceeds from 20 to 30 mg., small portions of the lead film are liable to become detached before the operation is completed, and, floating around in the acid solution, to be slowly re-dissolved.

"The result of many trials led me to experiment with the precipitation of lead as chromate under various conditions; and this method, as finally elaborated and tested, has proved so rapid and satisfactory in every way that I have discarded all other methods, and use this not only for small percentages of lead, but for all wet lead-assays, on whatever material.

"The insolubility of lead chromate in water, and in dilute acetic acid, is well-known, and the gravimetric method of estimation by chromatic precipitation has been in use to some extent for years. Modifications, looking to the development of this method into a volumetric one, have also been published; but the fact remains that, at the present time, the volumetric chromate method as a commercial wet lead method is practically unknown.

"Taking advantage of the reactions of lead chromate, together with such literature as bore upon the subject, preliminary trials were made. A solution of normal potassium chromate was generally used, although dichromate in some cases answers as well, the normal chromates being converted to dichromates on addition of acids; but as I have generally used the normal chromate for the precipitating solution and as its equations are somewhat simpler, I will consider it here.



"The potassium chromate solution is added in slight excess of the fine quantity necessary to precipitate all of the lead; the lead chromate is separated by filtration and washing; the filtrate containing the excess of chromate is acidified with about 25 cc. of dilute hydrochloric acid (1:1); a small crystal of potassium iodide (about 0.5 g.) is then added; and the liberated iodine is titrated with a standard solution of sodium hyposulphite in the usual manner, running-in the 'hypo' until the brown color of iodine is almost discharged. Then a few drops of starch paste are added, and the titration is continued until the blue color is just discharged, and a clear solution remains. The standard hyposulphite solution is preferably made of such a strength that 1 cc. will equal 0.5 cc of chromate solution, in order to afford an easy calculation of